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Electrical properties of donor- and acceptor-doped $BaBi_4Ti_4O_{15}$

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Abstract

The electrical properties of the $BaBi_4Ti_4O_{15}$ compound, a member of the family of Aurivillius bismuth-based layer-structure perovskites, have been studied as a function of aliovalent doping and processing conditions. The samples were prepared by reaction sintering or hot forging of a mixture of $BaTiO_3$ and $Bi_4Ti_3O_{12}$ with Nb substituted for Ti, as a donor dopant, and Fe as an acceptor. The dielectric constant of $BaBi_4Ti_4O_{15}$ is increased by both dopants. Nb doping decreases the Curie temperature, while Fe doping increases it. The conductivity of $BaBi_4Ti_4O_{15}$ is p-type and it is decreased by Nb doping and increased by Fe doping. The incorporation of aliovalent dopants into the $BaBi_4Ti_4O_{15}$ structure, is however, preferentially compensated by the change in the composition of the compound. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Dielectric properties; Electrical properties; Hot pressing; Titanates

1. Introduction

The compounds of the family of Aurivillius bismuth-based layer-structure perovskites are of technical interest due to their high-temperature ferroelectricity, in particular for high-temperature piezoelectric applications.

The structures of the Aurivillius family of compounds consist of $(Bi_2O_2)^{2+}$ layers interleaved with perovskite-like $(A_{n-1}B_nO_{3n+3})^{2-}$ layers. The grains in the compounds' ceramics have plate-like shape, with larger surfaces parallel to the $(Bi_2O_2)^{2+}$ layers. Their intrinsic electrical properties are anisotropic, with the maximum value of conductivity and the major component of spontaneous polarization parallel to the $(Bi_2O_2)^{2+}$ layers. As a result, properties of the polycrystalline materials are strongly affected by their microstructure, especially by the orientation of the plate-like grains and by the length-to-thickness ratio (aspect ratio) of the grains.[1,2]

As reported for compounds $Bi_4Ti_3O_{12}$[3] and $SrBi_4Ti_4O_{15}$[4], the Aurivillius family of compounds exhibits p-type electronic conductivity.

$BaBi_4Ti_4O_{15}$, as the $n=4$ member of the Aurivillius family has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite $(A_{n-1}B_nO_{3n+3})^{2-}$ block $((Bi_2O_2)^{2+}\cdot((BaBi_2)Ti_4O_{13})^{2-})$. It has a high Curie temperature of 417°C.[5]

In the present study, dielectric properties and the electrical resistivity of the $BaBi_4Ti_4O_{15}$ compound have been studied as a function of donor or acceptor doping and processing conditions.

2. Experimental

The samples were prepared by the reaction sintering of $BaTiO_3$, $Bi_4Ti_3O_{12}$ and appropriate dopants. $Bi_4Ti_3O_{12}$ was prepared by pre-reacting stoichiometric quantities of Bi_2O_3 (Alfa 17107) and TiO_2 (Bayer T) at 900°C. Nb^{5+} substituted for Ti^{4+} was used as a donor dopant and Fe^{3+} as an acceptor. Starting oxides: $BaTiO_3$ (Transelco 219/9), $Bi_4Ti_3O_{12}$, Bi_2O_3 and Nb_2O_5 or Fe_2O_3 were mixed in an agate ball mill in accordance with the nominal formulas $BaBi_4Ti_{4-4x}Nb_{4x}O_{15}$ and $BaBi_4Ti_{4-4x}Fe_{4x}O_{15}$, with the value of x ranging from 0 to 0.20 (0–20 mol% of dopant). The mixtures were pressed into pellets (6 mm in diameter and ~3 mm thick) and sintered for 1 h at 1100°C under different atmospheres (air, oxygen or pure N_2). Selected samples were hot forged at 1100°C for 1 h under an applied uniaxial pressure of 100 MPa in air.

The sintered pellets were electroded with a gallium/indium eutectic to provide the ohmic contacts. Resistivity

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vs. temperature was measured with a computerized instrument (Model 3457A, Hewlett-Packard, Mountain View, CA) and the capacitance with an Impedance Analyzer (Model 4192A LF, Hewlett-Packard, Mountain View, CA) at a frequency of 100 kHz.

The solid solubility of the dopants in $BaBi_4Ti_4O_{15}$ was studied using scanning electron microscopy (SEM, Jeol 5800) and X-ray powder diffractometry (XRPD, Simens D5000).

3. Results and discussion

Fig. 1 illustrates the influence of hot forging and doping on the grain size of $BaBi_4Ti_4O_{15}$ ceramics. The hot-forged samples had a grain size comparable with conventionally sintered materials, however, a low degree of ordering of the plate-like grains, perpendicular to the direction of forging, was visible. Hot forging is an effective method for the preparation of ceramics with a preferential grain orientation.[1] The dopants had different influences on the grain size of the samples. Whereas the Nb doping decreased the grain size of the $BaBi_4Ti_4O_{15}$ ceramics, Fe doping did not influence the grain growth significantly.

Fig. 2 shows the temperature dependence of the dielectric constant for undoped $BaBi_4Ti_4O_{15}$ samples, prepared by conventional sintering and by hot forging. The hot-forged samples were measured parallel (par) and perpendicular (per) to the direction of hot forging. The dielectric constant of the hot-forged material is much higher than that of the conventionally sintered material. This could be attributed to the higher density of the hot-forged material and to a change in the orientation of the plate-like grains during hot forging. The dielectric constant measured perpendicular to the direction of hot forging was much lower than that measured parallel to it, suggesting a larger dielectric constant perpendicular to the $(Bi_2O_2)^{2+}$ layers of the $BaBi_4Ti_4O_{15}$ structure. This is inconsistent with the largest spontaneous polarisation being parallel to the $(Bi_2O_2)^{2+}$ layers. The lower dielectric constant parallel to the $(Bi_2O_2)^{2+}$ layers can be explained by a much larger conductivity in this direction than perpendicular to it (see below).

Doping of $BaBi_4Ti_4O_{15}$ with Nb (Fig. 3) and with Fe (Fig. 4) changed the temperature of the dielectric-constant maximum (Curie temperature, T_C), strongly suggesting incorporation of the dopants into the $BaBi_4Ti_4O_{15}$ structure. Substitution of the Ti ions in the $BaBi_4Ti_4O_{15}$ structure by Nb ions decreases the Curie temperature (T_C) by approximately 7°C/mol% Nb_{Ti}, whereas substituting Fe for Ti increases the T_C by approximately 13°C/mol% Fe_{Ti}. Both dopants increased the room-temperature dielectric constant of $BaBi_4Ti_4O_{15}$ ceramics. The Nb doping changed the shape of the dielectric-constant maximum. Whereas the low Nb concentrations, up to 2 mol%, increased the dielectric constant at T_C, the higher Nb concentrations suppressed the dielectric-constant maximum. Broadening of the dielectric-constant maximum could be related to the changes in the microstructure with Nb doping, e.g. the appearance of secondary phases, the non-homogeneous distribution of dopants and/or the decrease in grain size (Fig. 1). With Fe doping, the dielectric constant increased for low dopant concentrations (up to 1 mol% Fe_{Ti}) and slowly decreased with higher Fe concentrations. However, the broadening of the maximum at high Fe concentrations was less pronounced than in the case of Nb doping.

As for the undoped material, doped hot-forged samples (measured parallel to the direction of hot forging) also had much higher dielectric constants than conventionally sintered materials (Fig. 3). The shift in T_C was larger for hot-forged samples than for sintered samples, suggesting that a larger concentration of dopant dissolved in the matrix phase during hot forging.

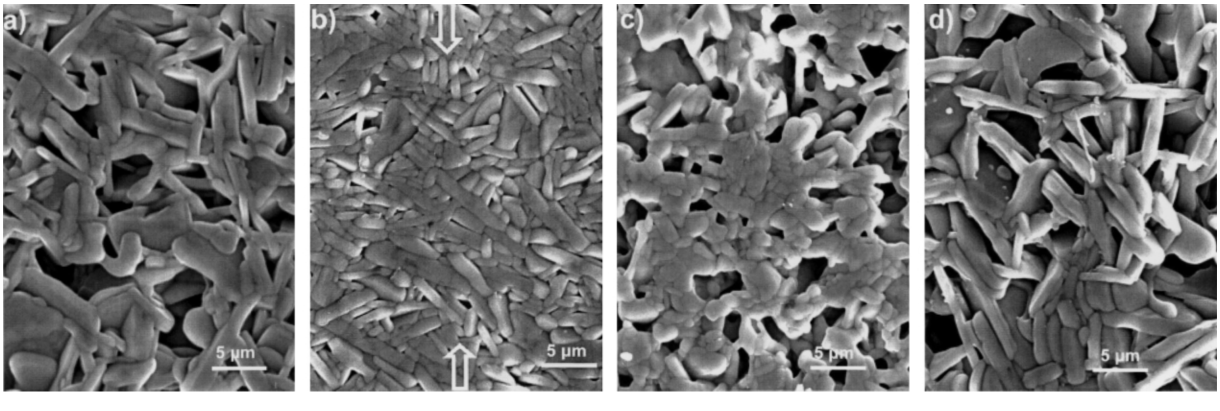

Fig. 1. Microstructures of: (a) conventionally sintered undoped $BaBi_4Ti_4O_{15}$ ceramics, (b) hot-forged undoped $BaBi_4Ti_4O_{15}$ ceramics (the direction of hot forging is marked by the arrow), (c) conventionally sintered 5 mol% Nb-doped $BaBi_4Ti_4O_{15}$ ceramics and (d) conventionally sintered 5 mol% Fe-doped $BaBi_4Ti_4O_{15}$ ceramics.

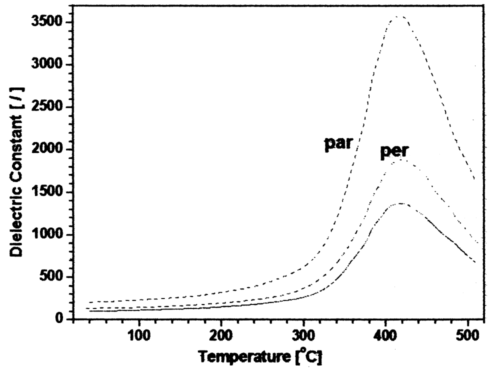

Fig. 2. Temperature dependence of dielectric constant for undoped $BaBi_4Ti_4O_{15}$ ceramics conventionally sintered (solid line) and hot forged (dashed line). The hot-forged sample was measured parallel (par) and perpendicular (per) to the direction of hot forging.

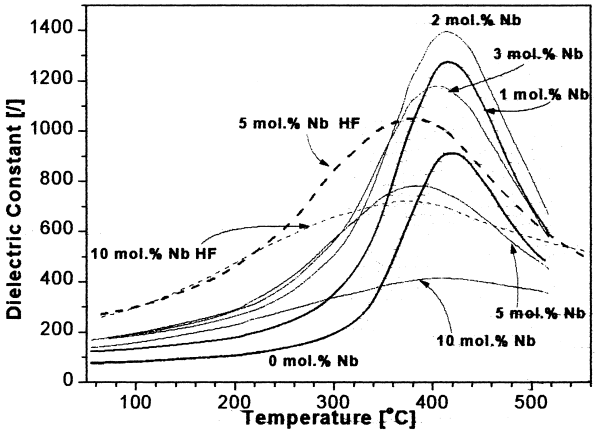

Fig. 3. Temperature dependence of dielectric constant for Nb-doped $BaBi_4Ti_4O_{15}$ ceramics. The samples were conventionally sintered (solid line) and hot forged (HF-dashed line).

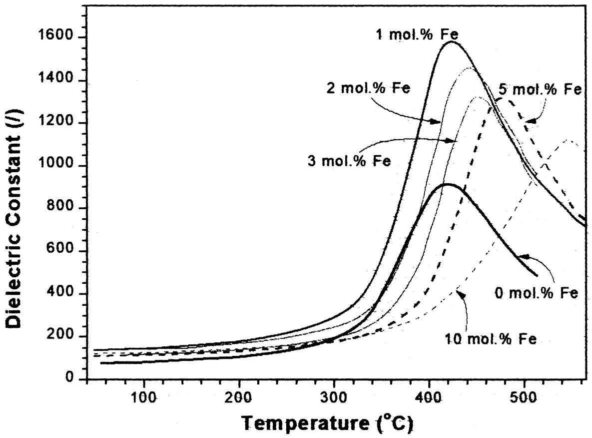

Fig. 4. Temperature dependence of dielectric constant for Fe-doped $BaBi_4Ti_4O_{15}$ ceramics prepared by conventional sintering.

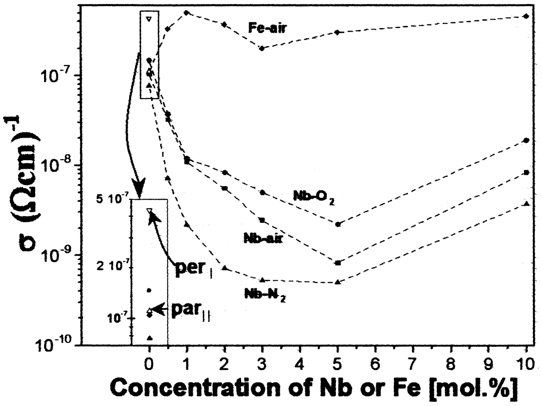

Fig. 5. The conductivity at 300°C as a function of dopant concentration and sintering atmosphere. The conductivity of hot-forged, undoped samples measured parallel (par) and perpendicular (per) to the direction of forging is also shown.

Fig. 5 shows the conductivity at 300°C for the $BaBi_4Ti_4O_{15}$ samples as a function of the method of sintering and aliovalent doping. Hot-forged samples (measured parallel and perpendicular to the direction of forging) showed higher conductivity than conventionally sintered samples, most probably due to their much higher density. The conductivity of the hot-forged samples was much lower parallel to the direction of hot forging than perpendicular to it. The result is in accordance with the lower conductivity of the compound perpendicular to the larger surfaces of the anisotropic plate-like grains. The undoped and Nb-doped samples were sintered in air, oxygen and pure nitrogen. The conductivity of the undoped samples increased after sintering in oxygen and decreased with sintering in nitrogen, in agreement with p-type electronic conductivity. Higher oxygen partial pressures promote formation of electron holes $h^{\bullet}$. In accordance with p-type conduction, the conductivity was increased by acceptor doping (Fe_{Ti}) and decreased by donor doping (Nb_{Ti}). Acceptors increase the concentration of electron holes, whereas donors decrease it. The conductivity decreased with donor doping to a minimum value where the concentration of electron holes matches the electron concentration ($p=n$). With a further increase in the donor concentration the conductivity becomes n-type and starts to increase again. The minimum conductivity appears at a lower donor concentration in nitrogen than in oxygen.

Fig. 6 shows the microstructures of the samples, which were annealed for 3 days at 1100°C after hot forging to achieve equilibrium. In the 5 mol% Nb-doped sample (Fig. 6a), no Nb-rich secondary phases were detected, proving that the solid solubility of Nb in $BaBi_4Ti_4O_{15}$ was not exceeded. However, in addition to the Nb-doped $BaBi_4Ti_4O_{15}$ matrix grains, the $Bi_4Ti_3O_{12}$ phase was also present, suggesting that the composition of the matrix phase was different from the nominal composition ($BaBi_4Ti_{4-4x}Nb_{4x}O_{15}$). In the 8 mol% Nb-doped sample (Fig. 6b), the solid solubility of Nb in the matrix phase was exceeded and a Nb-rich phase appeared together with the $Bi_4Ti_3O_{12}$ compound. X-ray diffractometry showed that reflections ascribed to the

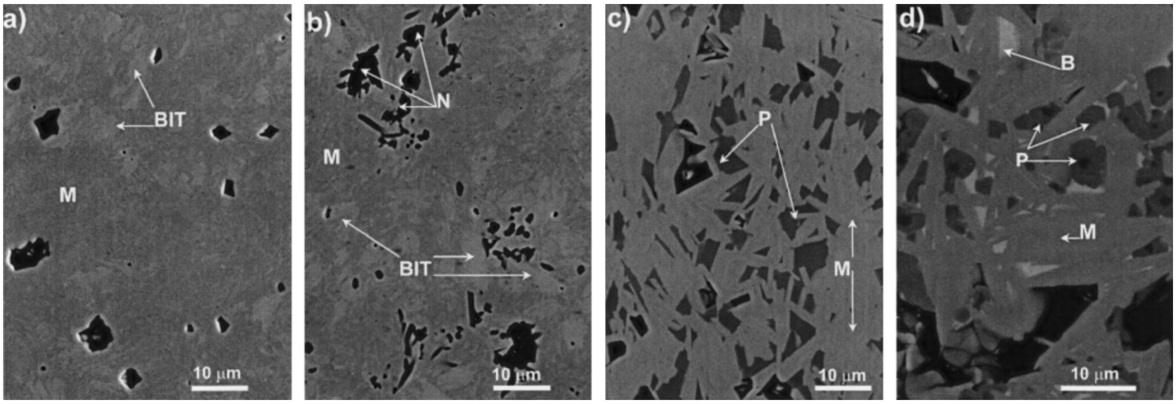

Fig. 6. Backscattered-electron micrographs showing: (a) microstructures of 5 mol% Nb-doped sample, (b) 8 mol% Nb-doped sample, (c) 12 mol% Fe-doped sample and (d) 20 mol% Fe-doped sample. (M: Nb- or Fe-doped $BaBi_4Ti_4O_{15}$ matrix phase; BIT: $Bi_4Ti_3O_{12}$; N: Nb-rich phase; P: Ba-rich phase with perovskite structure; B: Bi_2O_3).

Table 1

Compounds detected in the samples and composition of the $BaBi_4Ti_4O_{15}$ matrix phase. Phase composition of the samples was determined by the combination of X-ray diffractometry and SEM/EDS

		Composition of the matrix phase[a] (M)				
Sample	Identified[b] phases	Ba (at.%)	Bi (at.%)	Ti (at.%)	Nb or Fe (at.%)	Bi:Ba (at.%)
0 mol% Nb, Fe	M	4.12±0.19	16.95±0.23	16.46±0.31	–	4.12±0.15
5 mol% Nb-HF[c]	M, BIT	4.80±0.36	16.63±0.22	15.73±0.11	0.47±0.14	3.48±0.31
10 mol% Nb-HF	M, BIT, N	5.26±0.25	16.06±0.28	15.27±0.14	1.01±0.16	3.06±0.18
12 mol% Fe-HF	M, P	2.52±0.31	18.35±0.21	14.90±0.31	1.76±0.14	7.39±0.88
20 mol% Fe	M, P, B	2.13±0.08	18.88±0.13	14.19±0.07	2.39±0.16	8.89±0.39

[a] Oxygen at.% by difference.

[b] M: Nb- or Fe-doped $BaBi_4Ti_4O$ matrix phase; BIT: $Bi_4Ti_3O_{12}$, N: Nb-rich phase; P: Ba-rich phase with perovskite structure; B: Bi_2O_3).

[c] HF: hot forged.

Nb-rich phase match those of the $Ba_4Bi_2Ti_4Nb_6O_{30}$ compound.[6]

The sample doped with 12 mol% Fe (Fig. 6c) was composed of an Fe-doped $BaBi_4Ti_4O_{12}$ matrix phase and a Ba-rich phase with the perovskite structure, whereas in the 20 mol% Fe-doped sample (Fig. 6d), Bi_2O_3 was also observed. The Ba-rich perovskite phase was composed of Ba, Ti, Bi, Fe and O.

The matrix phase in undoped and doped samples has been analysed using EDS analysis (Table 1). Here, it should be noted that the analysis used has limited accuracy, primarily due to the overlapping of the Ba and Ti as well as Bi and Nb spectral lines.

However, when the results are compared, it could be concluded that the change of charge during incorporation of the aliovalent dopants into the $BaBi_4Ti_4O_{15}$ structure is compensated for by the change in composition in terms of the ratio of Ba to Bi (Table 1). While the analysis of the undoped samples agrees well with the nominal composition of $BaBi_4Ti_4O_{15}$, the analysis of the Nb-doped samples showed an increase in Ba concentration and a decrease in Bi concentration and the analysis of the Fe-doped samples a decrease in Ba concentration and an increase in Bi concentration. The Ba^{2+} and Bi^{3+} ions occupy the A sites in the $(A_{n-1}B_nO_{3n+3})^{2-}$ perovskite block of the Aurivillius-type layered structure. Most probably, the charge compensation during incorporation of the aliovalent dopant occurs as a consequence of the change in the Ba^{2+}/Bi^{3+} ratio at the A sites in the perovskite block. During donor incorporation, the Ba^{2+}/Bi^{3+} ratio is increased thus decreasing the average valency of the A sites, whereas during incorporation of the acceptors the Ba^{2+}/Bi^{3+} ratio is decreased. More accurate WDS microanalyses are currently in progress.

4. Conclusions

The dielectric constant of the $BaBi_4Ti_4O_{15}$ compound is increased when Nb or Fe substitute for Ti. Nb doping decreases the Curie temperature by approximately 7°C/mol%, whereas Fe doping increases the T_C by approximately 13°C/mol%. The $BaBi_4Ti_4O_{15}$ compound exhibits p-type electronic conductivity. It is increased by acceptor doping (Fe) and decreased by donor doping

(Nb). The change in the charge during the incorporation of aliovalent dopants into the $BaBi_4Ti_4O_{15}$ structure is preferentially compensated for by the change in the composition of the compound.

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